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**Unexpected Migratory Insertion Reactions of M(alkyl)₂ (M = Zn, Cd) with
Diamidocarbenes**

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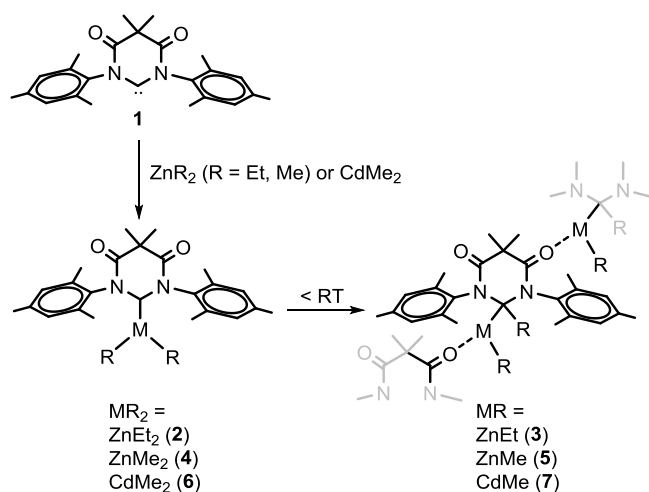
Abstract

The electrophilic character of free diamidocarbenes (DACs) allows them to activate inert bonds in small molecules, such as NH_3 and P_4 . Herein, we report that metal coordinated DACs also exhibit electrophilic reactivity, undergoing attack by Zn and Cd dialkyl precursors to afford the migratory insertion products $[(6\text{-MesDAC-R})\text{MR}]$ ($\text{M} = \text{Zn}, \text{Cd}$; $\text{R} = \text{Et}, \text{Me}$; $\text{Mes} = \text{mesityl}$). These species were formed via the spectroscopically characterised intermediates, $[(6\text{-MesDAC})\text{MR}_2]$, exhibiting barriers to migratory insertion which increase in the order $\text{MR}_2 = \text{ZnEt}_2 < \text{ZnMe}_2 < \text{CdMe}_2$. Compound $[(6\text{-MesDAC-Me})\text{CdMe}]$ showed limited stability, undergoing deposition of Cd metal, by an apparent $\beta\text{-H}$ elimination pathway. These results raise doubts about the suitability of diamidocarbenes as ligands in catalytic reactions involving metal species bearing nucleophilic ligands (M-R , M-H).

Diaminocarbenes have had a remarkable impact on the landscape of organometallic chemistry over the last decade, primarily because of their strong σ -donor properties which afford very stable M-C bonds.^[1] In an effort to try to enhance the strength of these M-C interactions, many groups have attempted to alter the donor (nucleophilic) as well as acceptor (electrophilic) character of carbenes by manipulation of the HOMO-LUMO gap.^[2] Arguably, cyclic alkyl amino carbenes (CAACs) and diamidocarbenes (DACs) have emerged as the most well-known and synthetically accessible of these derivatives.^[3] In the case of CAACs, electrophilicity is enhanced by the presence of only a single α -N atom, while DACs are made more electron-accepting by the incorporation of carbonyl groups adjacent to the ring N atoms (**1** in Scheme 1). The result is that both CAACs and DACs exhibit very different reactivity to diaminocarbenes, behaving more like traditional triplet carbenes in undergoing reactions with inert bonds (C-H, H-H, N-H, P-H, P-P) and coupling reactions with CO and isocyanides.^[4-6] At the same time, both CAACs and DACs retain enough nucleophilic character to act as two-electron donor ligands to a range of late d-block metal centers (Ru, Rh, Ir, Pd, Cu, Au).^[5,7] Herein, we report the first examples of metal bound diamidocarbene ligands exhibiting electrophilic reactivity with the observation that compounds of the type [(6-MesDAC)MR₂] (M = Zn, R = Et, Me; M = Cd, R = Me)^[8] undergo migratory insertion of an alkyl ligand onto the carbenic carbon.^[9,10] In the case of [(6-MesDAC)ZnEt₂], this process is extremely facile, taking place at temperatures as low as 211 K.

Upon addition of one equivalent of a 1.0 M heptane solution of ZnEt₂ to a THF solution of **1**, the instantaneous formation of a homogeneous red solution was observed which disappeared after a few seconds, and was replaced by a colourless, insoluble precipitate. This precipitate was characterized by X-ray crystallography as [(6-MesDAC-Et)ZnEt] (**3**, Scheme 1), the product of migratory insertion of one of the Zn-ethyl groups onto the DAC ligand. The structure showed that **3** was polymeric (Figure 1) by virtue of weak Zn←O interactions (Zn-

O = 2.166(3) Å) between neighbouring [(6-MesDAC-Et)ZnEt] units.^[11] IR spectroscopy provided further evidence for this interaction with the appearance of a low frequency (1576 cm⁻¹) CO stretch for the Zn bound carbonyl and a higher frequency band at 1651 cm⁻¹ for the unperturbed carbonyl group. As shown in Figure 1, the Zn←O interaction affords a T-shaped Zn center (C_{DAC-Et}-Zn-C 159.90(17)°; C_{DAC-Et}-Zn-O 99.50(14)°) bound to a single ethyl group (Zn-C 1.998(4) Å;^[12] *c.f.* 1.948(5) Å in ZnEt₂^[13]) and an sp³-hybridised carbon (Zn-C_{DAC-Et} 2.059(4) Å; N(1)-C(1)-N(2) 109.6(3)°; *c.f.* 127.72(18)° in **1**)^[6] formed via the migratory insertion process.



Scheme 1. Pathway to formation of migratory insertion products **3**, **5** and **7**.

Diffusion ordered (DOSY) NMR experiments suggested that **3** dissociates into a monomer in solution, on the basis of the good agreement between the value of 4.7 Å determined for the hydrodynamic radius (r_H , measured in CD₂Cl₂) and the value of 5.3 Å calculated for the monomeric unit of **3** from the solid-state structure ($r_{X\text{-ray}}$).^[14] The ¹H and ¹³C{¹H} NMR spectra showed resonances that were diagnostic of the migratory insertion process and the resultant de-symmetrisation of the six-membered heterocyclic ring. The Zn-bound ethyl group exhibited two resonances in the ¹H NMR spectrum (CH₂, δ = 0.00 ppm;

CH₃, δ = 0.84 ppm) at lower frequency than those of the migrated ethyl group (CH₂, δ = 0.73 ppm; CH₃, δ = 2.27 ppm). This correlated in a ¹H-¹³C HMBC spectrum to a resonance arising from the quaternary NCN carbon at δ = 88.0 ppm.^[15]

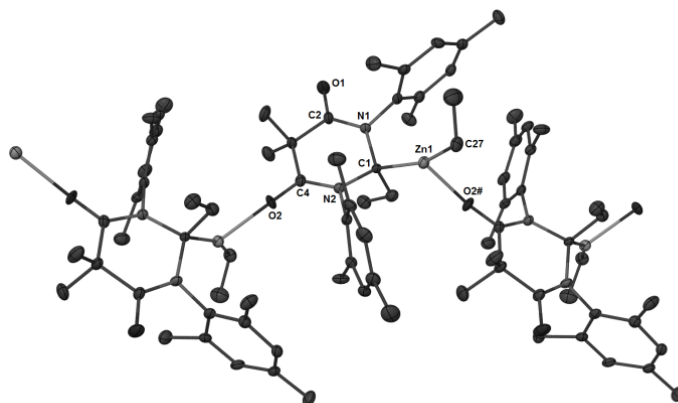


Figure 1. Molecular structure of **3**. Ellipsoids are shown at the 50% level. All hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [deg]: Zn(1)-C(1) 2.059(4), Zn(1)-C(27) 1.998(4), Zn(1)-O(2#) 2.166(3), C(2)-O(1) 1.230(5), C(4)-O(2) 1.238(5), C(1)-Zn(1)-C(27) 159.90(17), C(1)-Zn(1)-O(2#) 99.50(14), N(1)-C(1)-N(2) 109.6(3). # atoms generated by symmetry operation $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

When ZnEt₂ was added to a cold (178 K) [D₈]-THF solution of 6-MesDAC, the intermediate responsible for the red colour was stabilized indefinitely, allowing its spectroscopic characterization as the Zn diamidocarbene adduct, [(6-MesDAC)ZnEt₂] (**2**, Scheme 1).^[16] This displayed CH₂ and CH₃ proton resonances at δ = -0.48 ppm and δ = 0.70 ppm, respectively, which integrated in a ratio of 4:6:4 with a signal at δ = 7.05 ppm for the four aromatic protons of the mesityl rings of 6-MesDAC, confirming the 2:1 ratio of Et:6-MesDAC ligands. The ¹³C signal for the Zn-carbene resonated at *ca.* δ = 236 ppm. Upon warming the sample above 211 K, the NMR signals for **2** rapidly disappeared and, indeed,

removal of the NMR tube from the spectrometer at this temperature revealed the characteristic colourless precipitate of **3**.

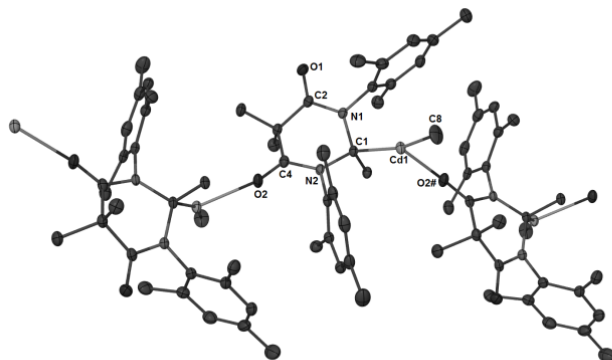
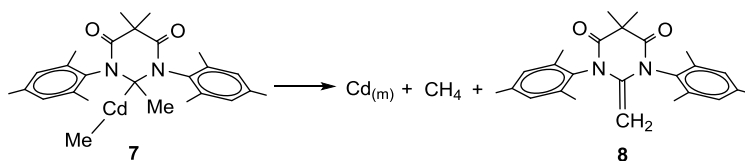


Figure 2. Molecular structure of **7**. Ellipsoids are shown at the 20% level. Solvent and hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [deg]: Cd(1)-C(1) 2.197(6), Cd(1)-C(8) 2.107(8), Cd(1)-O(2#) 2.416(5), C(2)-O(1) 1.226(8), C(4)-O(2) 1.227(8), C(1)-Cd(1)-C(8) 162.1(3), C(1)-Cd(1)-O(2#) 95.50(19), N(1)-C(1)-N(2) 108.0(4). # atoms generated by symmetry operation $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Analogous low temperature experiments with ZnMe_2 or CdMe_2 and **1** (Scheme 1) gave yellow rather than red solutions, but comparable spectroscopic data to **2** (**4**: ZnCH_3 : $\delta = -1.40$ (^1H), $\delta = -9.1$ ppm (^{13}C); $\text{Zn-C}_6\text{-MesDAC}$: $\delta = 237.6$ ppm (^{13}C); **6**: CdCH_3 : $\delta = -1.12$ (^1H), $\delta = -7.9$ ppm (^{13}C); $\text{Cd-C}_6\text{-MesDAC}$: $\delta = 252.9$ (^{13}C)).^[17] Higher barriers were found for the subsequent migratory insertion reactions, with the Zn and Cd products **5** and **7** being formed at 245 and 267 K respectively.^[18] X-ray crystallography showed that **7** was polymeric in the solid-state (Figure 2) although, unsurprisingly, both the Cd←O (2.416(5) Å) and Cd-C (Cd(1)-C(1) 2.197(6), Cd(1)-C(8) 2.107(8) Å) distances were longer than in the Zn species (Figure 2).^[19] Analysis of both structures revealed substantial distortions from planarity with respect to the carbene mesityl substituents. This is evidenced by the distances of the *ortho*

methyl carbon atoms from the mean planes of the phenyl rings to which each is bonded. These distances range from 0.20 to 0.28 Å (in **3**) and 0.20 to 0.23 Å (in **7**). In all cases, the methyl groups lean towards the carbonyl groups. Space filling models suggest steric clashes between the latter and the *ipso* carbons of proximate mesityl functionalities. This appears to induce some slight ring puckering in the solid state, the effect of which is exaggerated by the methyl deviations quoted herein. DOSY measurements on **7** once more supported a monomeric structure in solution ($r_{\text{H}} = 4.9$ Å, $r_{\text{X-ray}} = 5.5$ Å).^[14]

Significant differences were observed in the solution behavior of **3**, **5** and **7**. Whereas **3** was fully soluble and indefinitely stable in CD₂Cl₂ under anaerobic conditions (even up to 323 K), the methyl analogue, **5**, proved to be only partially soluble in the same solvent even at 313 K. This enabled ¹H NMR data to be recorded, but efforts to record complete ¹³C data proved fruitless as the compound decomposed over a period of hours. In the case of the Cd complex **7**, dilute and totally homogeneous dichloromethane solutions were stable, although attempts to crystallize the compound from saturated solutions resulted in quantitative decomposition over 12-24 h, with deposition of metallic Cd (confirmed by powder X-ray diffraction)^[20] and elimination of methane and the known exocyclic alkene **8** (Scheme 2). This was characterized by the appearance of a diagnostic vinylic ¹H NMR signal at $\delta = 3.25$ ppm.^[41] In light of the heterogeneous conditions necessary for the decomposition of **7**, the exact mechanism remains unclear, although β -H elimination from the C-bound methyl group onto Cd, followed by reductive elimination of CH₄ from a putative Cd methyl hydride intermediate appears most probable.



Scheme 2. Decomposition reaction of [(6-MesDAC-Me)CdMe], **7**.

In summary, we have described the first examples of electrophilic reactivity being observed in metal coordinated diamidocarbene (DAC) ligands with the observation of migratory insertion reactions of Zn and Cd alkyl groups. These processes proceed via (DAC)MR₂ intermediates, which are only stable below room temperature, undergoing migratory insertion between 211 and 267 K. These findings could have implications for the stability of metal DAC species under catalytic conditions in which metal alkyl or metal hydride groups are also present. Given our interest in metal DAC catalysis,^[21] we are endeavouring to investigate this in more detail.

Acknowledgement. We acknowledge the University of Bath (LRC) and EPSRC (IMR) for financial support. We thank Dr. Andrew Johnson for the gifts of ZnMe₂ and CdMe₂, Dr Sam Cosham and David Stanton for experimental assistance, Dr John Lowe for NMR help and Prof Mark Weller for X-ray powder data.

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Scheme 1. Pathway to formation of migratory insertion products **3**, **5** and **7**.

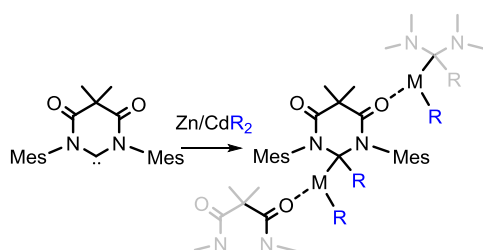
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Figure 2. Molecular structure of **7**. Ellipsoids are shown at the 20% level. Solvent and hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [deg] in **7**: Cd(1)-C(1) 2.197(6), Cd(1)-C(8) 2.107(8), Cd(1)-O(2#) 2.416(5), C(2)-O(1) 1.226(8), C(4)-O(2) 1.227(8), C(1)-Cd(1)-C(8) 162.1(3), C(1)-Cd(1)-O(2#) 95.50(19), N(1)-C(1)-N(2) 108.0(4). # Atoms generated by symmetry operation $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Scheme 2. Decomposition reaction of [(6-MesDAC-Me)CdMe], **7**.

Table of Contents Entry

Retention of electrophilic character by the diamidocarbene 6-MesDAC (Mes = mesityl; DAC = diamidocarbene) in the adducts [(6-MesDAC)MR₂] (MR₂ = ZnEt₂, ZnMe₂, CdMe₂) results in migratory insertion reactions to generate [(6-MesDAC-R)MR]. The ease of migratory insertion follows the order ZnEt₂ > ZnMe₂ > CdMe₂, occurring well below room temperature in all cases (see scheme).



Keywords: alkyl ligands; cadmium; diamidocarbenes; migratory insertion; zinc